

Responses to questions that EAD has received concerning hexavalent chromium ("chromium 6") in the method update rule (MUR)

### **Hierarchy of holding times between footnotes to Table II and in approved methods**

**Question:** Table IB (page 11218) lists the EPA Method for Chromium VI dissolved as 218.6, Rev.3.3 (1994). In Table II (page 11236) the maximum holding time for Chromium VI is listed as 28 days with a reference to footnote 20. Footnote 20 (page 11239) refers to the use of the ammonium sulfate buffer solution described in the Method at Sections 7.9 and 8.2. However, Section 1.4 of the same Method states [that samples must be] "analyzed within 24 hours of collection." The question is, which holding time is correct for Method 218.6? And, with respect to the non-EPA methods for Chromium VI listed in Table IB, is it also possible to have a 28 day holding time for these methods by using ammonium sulfate buffer as a preservative at the time of sample collection?

**Response:** Footnote 20 states: "To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed." The footnote supersedes the holding time in the approved methods, unless the longer holding time would compromise measurement of chromium 6, in which case the holding time in the method must be used. The footnote applies to all approved methods (e.g., Standard Methods, ASTM methods).

Please notice also footnote 4 to Table II, which states, in part: "Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid (e.g., samples analyzed for fecal coliforms may be held up to 6 hours prior to commencing analysis)... "Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See § 136.3(e) for details..." Therefore, if it is known that the chromium 6 concentration would change in less time than the 28 days allowed by footnote 20, or in less time than allowed in the approved method (e.g., 24 hours in Method 218.6), the sample must be held no longer than the time necessary to assure that the chromium 6 concentration does not change.

### **Interpretation of holding time requirement**

**Question:** Does footnote 20 to Table II mean that chemical preservation is the only option available and the resulting hold time is 28-days (i.e. unable to analyze unpreserved within 24-hours), or does it mean that chemical preservation is an option available in order to achieve a longer hold time but if you do not apply the 28-day holding time (i.e. analyze within 24-hours) then unpreserved is still acceptable?

**Answer:** Footnote 20 allows the holding time to be extended to 28 days at the option of the permittee, discharger, or monitoring laboratory, provided the sample is preserved as specified in the footnote. If desired, the sample may be held for no more than 24 hours unpreserved, as specified in the approved methods. Also, as stated in footnote 4 to Table II, "... A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability..."

**Disparity between holding times for drinking water and wastewater**

**Question:** EPA Method 218.6 for drinking water requires a 24-hour holding time, whereas footnote 20 to Table II at part 136 for wastewater allows 28 days when properly preserved, and the footnote supersedes the methods, so the footnote is applicable to Standard methods also. What this means is that drinking water and wastewater are regulated using the same methods but the holding times are different. Another example of this would disparity would be for PCBs where the method says one thing but the holding time table says another.

**Response:** You are correct in that there can be disparities between requirements for drinking water and wastewater and disparities between requirements in the holding time table at 40 CFR part 136 and in approved methods.

Regarding the disparity between requirements for chromium 6 for drinking water and wastewater, EPA received a request and data supporting a change of holding time to 28 days for chromium 6 in wastewater, proposed the change in the *Federal Register* on April 6, 2004 (69 FR 18165), and approved the change on March 12, 2007 (72 FR 11199). EPA did not receive a request and data supporting a change of holding time for drinking water and, therefore, did not change the holding time for drinking water. If EPA receives a request and supporting data for a change to the holding time for drinking water in the future, EPA will consider the request and data for the change in holding time for drinking water.

Regarding disparities between holding times in Table II at part 136 and in approved methods, holding time requirements in Table II apply to all approved methods, not just to EPA methods. Also, when information becomes available about an improvement in a requirement for a holding time, it is more straightforward to change Table II than to revise all approved methods. When an EPA method is revised, EPA attempts to correct the preservation and holding time to be consistent with Table II.

**Holding time for colorimetric methods**

**Question:** We use Standard Methods 3500-Cr D, which is a colorimetric method, and are not sure if our method is compatible with the change in preservation requirement in Table II. We assume that it is compatible because the method we use is still approved for NPDES and there is no alternative for Cr6+ in Table II. We have done some preliminary work using the buffer with our method and what immediately stands out is a shift in the curve. Is there any supporting information about using the buffer from method 218.6 with other Cr6+ methods?

**Answer:** At present, there is no supporting information about using the buffer with methods other than ion chromatography method 218.6. We suggest that you make up your standard solutions using the buffer and produce a calibration curve with the buffered solutions. If that does not work, do not use the buffer and return to requirements in the method (24-hour holding time, unpreserved), as provided for in footnote 20 to Table II.

**Information supporting holding time change**

**Question:** Since the Methods Update Rule was published on March 12, the Office of Solid Waste Methods Information Communication Exchange (MICE) Hotline has received several phone calls inquiring whether or not OSW will make such a change to Method 7199 determining hexavalent chromium in drinking water, groundwater and industrial wastewater effluents by IC, which is similar to your Method 218.6 "Chromium, Dissolved Hexavalent by IC". Would you

please provide a copy of the information and/or data that you have to make the change?

**Answer:** The information was provided in the Docket at proposal (see the proposal at 69 FR 18184, April 6, 2004 and the Docket at <http://www.regulations.gov>. Search "All Documents," "Environmental Protection Agency," and "OW-2003-0070" as the Keyword or ID. The link will be on page 3 at EPA-HQ-OW-2003-0070-0070).

### **Sample filtration**

**Question:** There is a requirement in EPA Method 218.6 to filter the sample prior to adding the buffer. However, the MUR makes no mention of filtration when preserving the sample. It does however, say that the "new" requirements supercede the method requirements. Is filtration required prior to preservation for EPA 218.6 to enable the 28 day holding time?

**Response:** Yes, filtration is required immediately (within 15 minutes of collection) to prevent interconversion of chromium species. The supersession requirement applies to preservation and holding time only.

### **Volume of buffer solution required to reach the specified pH range**

**Question:** We (the Hampton Roads Sanitary District; HRSD) used the buffer solution described in Section 7.9 of Method 218.6, Rev. 3.3. Section 8.2 of Method 218.6, Rev. 3.3 states "Adjust the pH of the sample to 9-9.5 by adding dropwise a solution of the buffer." while Table II states the pH range as 9.3-9.7. HRSD typically uses Standard Methods 18th Ed. 3500-Cr D (colorimetric - diphenyl carbazide) for analysis, requiring a sample volume of one liter. HRSD experimented with the preservation technique specified in Footnote 20 of Table II. We found that for one liter of sample, 250 to 300 mL of buffer solution was needed in order to obtain a pH of 9.00 to 9.20. The minimum pH of 9.3 was not achievable even with the addition of large volumes of buffer solution. Since Section 8.2 of Method 218.6, Rev. 3.3 states that the buffer should be added dropwise, we are concerned that the buffer solution currently listed in Method 218.6, Rev. 3.3 may be incorrect. We are also concerned that the addition of 250 to 300 mL, or more, of the buffer solution to a one-liter sample would compromise the sample integrity since a dilution factor of 25-30% would be required. It would also be helpful if EPA would provide an explanation regarding narrowing the pH range from 9-9.5 to 9.3-9.7.

**Response:** EPA's Engineering and Analysis Division (EAD) contacted Elizabeth Hedrick at EPA's laboratory in Cincinnati, Ohio. Ms. Hedrick was one of the developers of EPA Method 218.6. Ms. Hedrick stated that EPA Method 218.6 was developed for dissolved chromium 6 in drinking water, and the buffering capacity of wastewaters may require a large volume of buffer.

EAD also contacted HRSD concerning possible use of sodium hydroxide (NaOH) for pH adjustment, based on use of NaOH in EPA Sampling Method 1669 (not promulgated). HRSD tested the 50% solution suggested in EPA Method 1669 and found the NaOH solution to be so concentrated that the pH overshoot the specified pH range when a very small volume was added. HRSD tested more dilute solutions of NaOH. Based on HRSD's tests, EPA suggests use of a 1% NaOH solution and believes that a few mL would be required to raise the pH from 7 to the specified pH range. EAD checked with Ms Hedrick about use of NaOH for pH adjustment. Ms Hedrick stated that, although NaOH would be acceptable from the standpoint of raising the pH, only the highest purity NaOH should be used, because NaOH can contain traces of chromium 6.

Based on testing by HRSD and statements by Ms Hedrick, EPA suggests use of the buffer in Section 7 of EPA Method 218.6 if the pH range can be achieved with sample dilution by no more than 10%. If the pH range cannot be achieved without diluting the sample by more than

10%, EPA suggests use of a minimum amount of NaOH solution, supplemented by buffer solution if necessary.

Regarding the disparity in pH ranges between EPA Method 218.6 (pH 9 - 9.5) and footnote 20 to Table II at part 136 (pH 9.3 - 9.7), EPA cannot locate the source for the requirement in footnote 20. EPA proposed the pH range of 9.3 - 9.7 in the method update rule proposal (April 6, 2004; 69 FR 18165) and received no comment on the 9.3 - 9.7 pH range. Therefore, the pH range of 9.3 - 9.7 must be met when the holding time is extended by use of NaOH or the buffer solution in Section 7.9 of EPA Method 218.6.